Microstructural Characterization of Electroless Ni-B

Final Report

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Summary

UCT Coatings, Inc. supplied Ni-B coatings were characterized experimentally. Techniques used included microhardness, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and x-ray diffraction (XRD), including heat treatment, hot stage and small angle x-ray scattering (SAXS).

The mounted heat treated nickel boron coating (provided by UTC Coatings) shows a 49% increase in microhardness over its companion non-heat treated specimen.

Plan view and cross sectional SEM micrographs display a "cauliflower-like," nodular microstructure for non-heat treated ("as-received") samples. Coating microstructures appear similar to zone I morphologies described in the literature. These consist of "columnar" structures (~200 to 500 nm in diameter that are not grains) aligned normal to the coating surface separated by non-dense boundaries. Small angle x-ray scattering confirms this large scale morphology.

XRD patterns of all "as-received" samples display broad "amorphous humps" indicative of amorphous/nano-crystalline structure with small superimposed Bragg reflections. One or more of these are due to crystalline Ni, whereas the others are unidentified. The "amorphous humps" persisted through all heat treatments although Bragg peaks of various phases grew relative to the "amorphous humps" as heat treatment temperatures increased.

Three samples (two of similar composition and one containing high relative amounts of Pb) were subjected to heat treatments to 200 C/392^{o}F, 225 C\437 ^{o}F, 250 C/482 ^{o}F, 275 C/527 ^{o}F, 300 C/572 ^{o}F, 325 C/617 ^{o}F, 350 C/662 ^{o}F and 385 C/725 ^{o}F in nitrogen. XRD was performed on each of the heat treated samples.

Heat treatment to the highest temperature resulted in the formation of Ni_3B and crystalline Ni, with some amorphous or nanocrystalline material remaining.

DSC indicates broad, shallow exothermic peaks ~100 C/212 ^{o}F to ~ 200 C/392 ^{o}F that disappear after heat treatments at lower temperatures. The different higher temperature behavior of the various samples is striking. Some display a single symmetric DSC peak, indicative, perhaps, of a single reaction. Others display various forms of two peaks, either separate and non-overlapping (high Pb content sample); overlapping but resolved; or overlapping but unresolved (the smaller appearing as a shoulder on the larger).

In addition to either amorphous or nano-crystalline material, Ni_3B was present in all samples heat treated to at least 300 C /572^{o}F.

Crystalline Pb was detected after all heat treatments (300 C /572^{o}F minimum), of the high Pb content sample.

Several unidentified crystalline phases were present in small amounts in some samples.

Introduction

Data collected throughout the 12 month project are reported and analyzed. All samples were provided by UCT Coatings in the form of flakes of as-deposited coatings removed from substrates.

In addition to characterizing "as-received" samples, samples were subjected to heat treatments that terminate at various temperatures beneath, and at, the final temperature to which UCT Coatings heat treats its electroless Ni-B coatings. These samples were characterized following the partial heat treatments. Characterization methods included microhardness measurements, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and x-ray diffraction (θ-2θ, hot stage and small angle x-ray scattering).

Experimental Procedures

Differential scanning calorimetry (DSC), x-ray diffraction (XRD), hot stage XRD, SAXS, microhardness, scanning electron microscopy (SEM), and energy dispersive x-ray diffraction (EDS) were performed on samples received from UCT Coatings. Table 1 lists the samples tested.

Differential Scanning Calorimetry

Differential scanning calorimetry was performed with a TA Instruments DSC-Q100 shown in figure 1 below. Nitrogen gas was flowed through the sample chamber at 10mL/min, and sample sizes ranged from 8mg to 50mg of particulate nickel boron samples. Samples were heated from 25 C/ 77°F to 385 C/725°F at a rate of 4°C/7.2°F per min. They were then held isothermally at 385 C/725°F for 5 minutes and cooled at a rate of 1.2°C/2.2°F per min to 25 C/77°F. After several replications, the cool down period was decreased to shorten the experiment from seven hours to 1 and one-half hours. Data from the cool down period show no relevance to the experiment. The onset temperatures of DSC peaks were determined by intersecting tangent lines with TA Instruments Universal Analysis software. Sample 2/5/2010 T2/S1 had a high lead content and was ramped at 4 C/7.2°F per min to 400 C/752°F in order to see the entire high temperature exothermic peak.

Figure 1: TA Instruments DSC-Q100

Table 1: Samples Tested

Sample ID	B wt%	Pb wt%	Ni wt%	Heat Treatment?	XRD	DSC	SEM	Micro hardness	Hot Stage XRD	SAXS
6/16 T2/S1	6.66	0.56	92.78	None	yes	yes	yes	yes		
				200 C/392°F	yes	yes				
				225 C\437 °F	yes	yes				
				250 C/482 °F	yes	yes				
				385 C/725 °F mounted sample				yes		
2/4/2010 T1/S2	6.4	0.57	93.03	None	yes	yes	yes			yes
				200 C/392°F		yes				
				225 C\437 °F		yes				
				250 C/482 °F		yes				
				275 C/527 °F		yes				
				300 C/572 °F	yes	yes				
				325 C/617 °F	yes	yes				
				350 C/662 °F	yes	yes				
				385 C/725 °F	yes	yes				
2/5/2010 T2/S1	6.29	2.08	91.63	None	yes	yes				yes
				200 C/392°F		yes				
				225 C\437 °F		yes				
				250 C/482 °F		yes				
				275 C/527 °F		yes				
				300 C/572 °F	yes	yes				
				325 C/617 °F	yes	yes				
				350 C/662 °F	yes	yes				
				385 C/725 °F	yes	yes				
2/8/2010 T2/S1	6.06	0.58	93.36	None	yes	yes	yes			yes
				200 C/392°F		yes				
				225 C\437 °F		yes				
				250 C/482 °F		yes				
				275 C/527 °F		yes				
				300 C/572 °F	yes	yes				
				325 C/617 °F	yes	yes				
				350 C/662 °F	yes	yes				
				385 C/725 °F	yes	yes				
12/8/2009 T2/S2	6.11	0.72	93.17	None		yes			yes	yes
12/14/2009 T1/S2	5.98	0.67	93.35	None		yes				yes
3/1/2010 T1/S1	6.17	0.61	93.22	None		yes				
1/18/2010 T2/S1	6.23	0.73	93.04	None		yes				yes

Heat Treatment
Heat treatments were performed on the "as-received" samples in an MTI tube furnace with flowing nitrogen gas. The samples were heated at 4°C/7.2°F per min to the final temperature; the samples were not held isothermally, but rather immediately furnace cooled to room temperature.

Samples 2/4/2010 T1/S2, 2/5/2010 T2/S1, and 2/8/2010 T2/S1 were each divided nine equal parts. Each sample was individually heat treated to one of the temperatures listed in table 1 above.

Microhardness
Microhardness measurements were performed on the mounted sample CERT 61609 T2/S1 with a LECO MHT Series 200 microhardness tester. CERT 61609 T2/S1 is two mounted cross sections of carbon steel coated with nickel boron – one sample heat treated to 725°F and one sample "as-received" with no heat treatment. Microhardness measurements were taken in Knoop with 25gf, 10 second dwell. Indentations were taken at evenly spaced intervals on the coating as shown in Figure 2. 10 indentions were made on each side of the cross section, totaling 20 repetitions per sample.

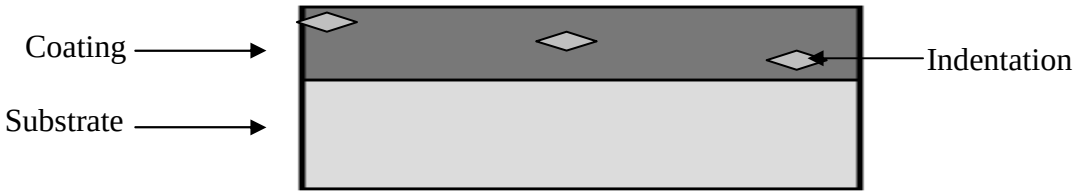


Figure 2: Schematic of microhardness indentation spacing shown in cross section (half of the double mounted sample is depicted).

X-ray Diffraction
An X'Pert PRO Alpha-1 diffractometer was used to collect θ-2θ scattering data (Brsagg-Brentano geometry). This machine utilized a 1.8kW ceramic copper x-ray source. An incident anti-scatter slit of 1/2° with a divergent slit of 1/4° were used along with 0.04rad Soller slits, a 10mm or 15mm mask, and a 5.0mm receiving anti-scatter slit. These devices focus the x-ray beam and improve resolution of peaks.

XRD samples were ground with a mortar and pestle and scanned from 2θ=25° to 80°. The step size was 0.033°, and a time/step of 500 seconds. The changeable optics in the machine were held constant for such scans

Occasionally, the 0.04rad Soller slits were removed to intensify and resolve peaks. XRD was performed over 2θ=10° to 80°, step size 0.0167°, and time/step of 45 seconds. X-ray diffraction was performed on the samples show in Table 2 below.

Several extended scans were taken of non-heat treated samples over 2θ=20° to 100°, step size 0.01675°, and time/step of 2,093 seconds. These data were analyzed for percent crystallinity and grain size.

XRD data were analyzed using X'Pert HighScore Plus (version 2.2b(2.2.2)) software produced by PANanalytic B.V. in conjunction with the ICDD PDF-4+ 2010 powder diffraction database. Analyses included peak search/I.D. and Rietveld fitting/refinement of whole diffraction patterns.

The extended patterns were analyzed using the peak fitting capabilities of MDI JADE 9 XRD software v. 9.1.5.

Small Angle X-Ray Scattering (SAXS)
Six samples were examined for x-ray scattering at small angles using Cu Kα radiation (λ = 1.5418 Å); a collimator/detector separation of 700 mm; exposure times of 3600 sec. One or more sample flakes were aligned such that the x-ray beam was incident normal to the plane of the coatings.

Hot Stage X-ray Diffraction
An X'Pert PRO MPD diffractometer with an Anton-Paar HTK2000 platinum strip furnace was used to analyze crystalline phase growth of nickel boron samples during heat treatments. The machine was calibrated with 1.8 kW Co Kα radiation. X-ray diffraction was performed at room temperature, 200 C/392°F, 225 C/437°F, 250 C/482°F, 275 C/527°F, 300 C/572°F, 325 C/617°F, 350 C/662°F, and 385 C/725°F with sample 12/08/2009 T2/S2 over the following 2-theta ranges: 42-45°, 50-56°, 59-63°, and 89-93°. Data collection occurs during thermal holds that allow overaging.

Scanning Electron Microscopy/Energy-Dispersive X-ray Spectroscopy

SEM images were captured with a LEO 1530 microscope with a field emission gun. Particulate samples were mounted flat and edge-on using carbon tape.

Samples were examined using an EDS attachment in a Hitachi S-3700N Variable Pressure SEM. Compositions of the top (defined as displaying a nodular structure), bottom (appearing relatively featureless, flat and without a nodular structure), and cross section/fracture surface (using a linescan) of the coatings were determined at a series of heat treatments (room temperature, 200 C/392°F, 225 C/437°F, 250 C/482°F, 275 C/527°F, 300 C/572°F, 325 C/617°F, 350 C/662°F, and 385 C/725°F).

Results

Scanning Electron Microscopy

Figures 19 and 20 display plan view and cross sectional SEM micrographs of sample 6/16 T2/S1 in the non-heat treated ("as-received") condition at various magnifications. Figure 21 is an SEM micrograph of sample 2/8/2010 T2/S1, and figure 22 displays images of the edge of sample 2/4/2010 T1/S2 in the non-heat treated ("as-received") condition.

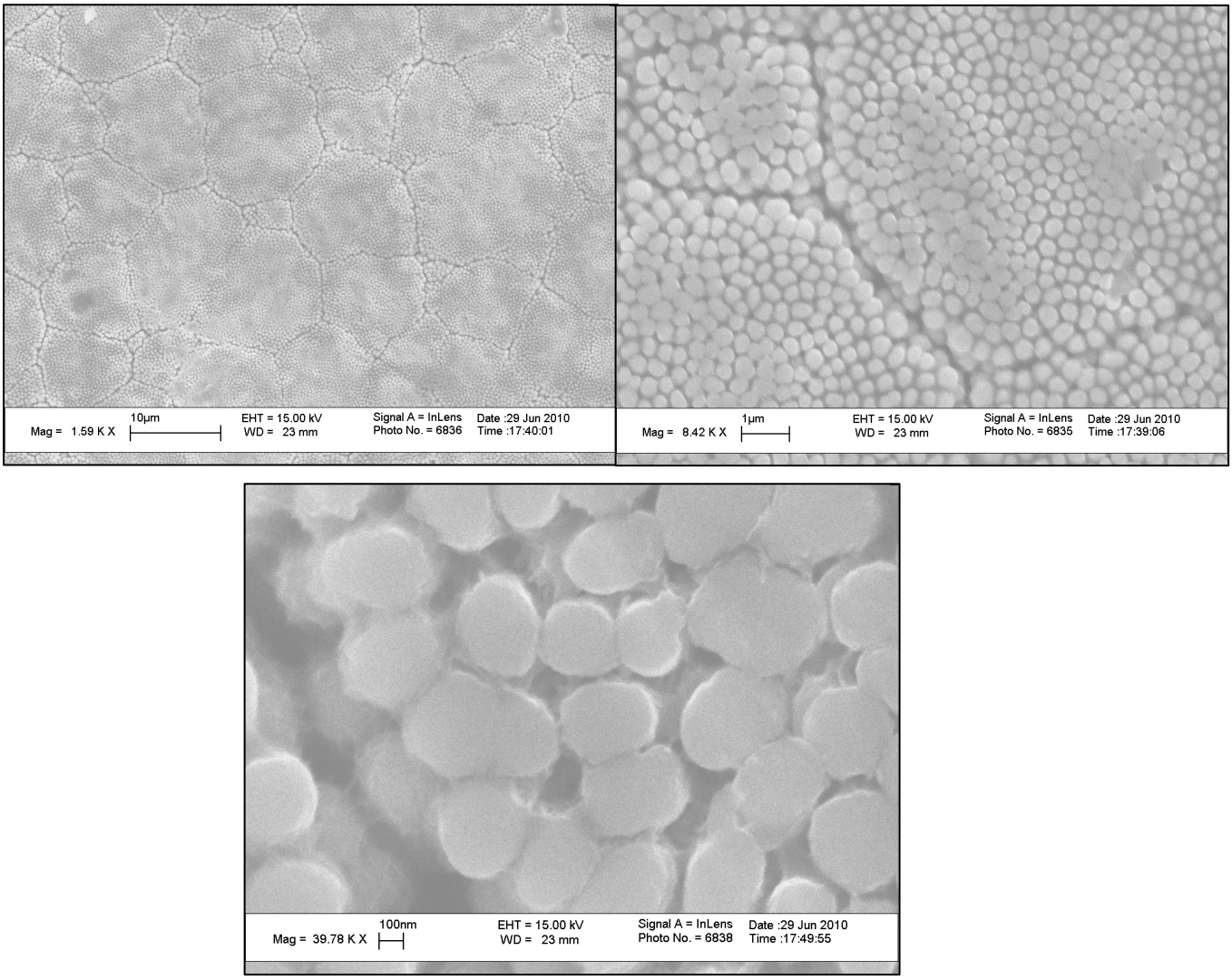


Figure 19: Plan View SEM Micrographs of sample 6/16 T2/S1 "as-received" taken at various magnifications. "Cauliflower-like" morphology is evident at the lowest magnification.

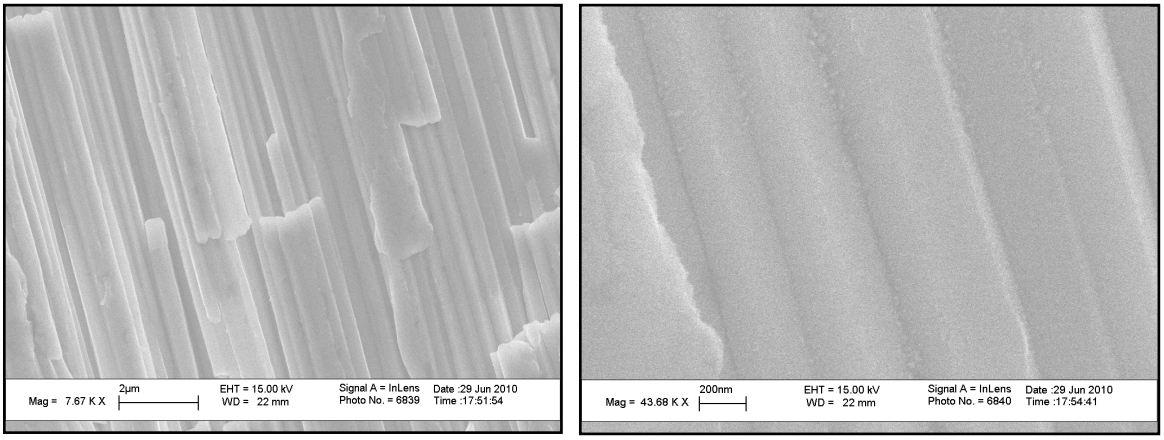


Figure 20: Cross Sectional SEM Micrographs of sample 6/16 T2/S1 "as-received" at two magnifications showing zone I microstructure.

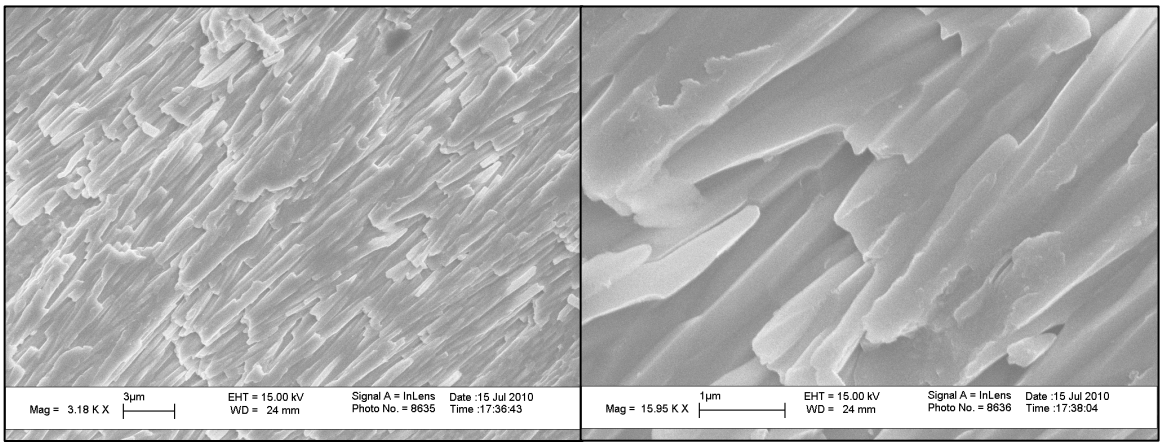


Figure 21: Cross Sectional SEM Micrographs of sample 2/8/2010 T2/S1 "as-received" at two magnifications showing zone I microstructure.

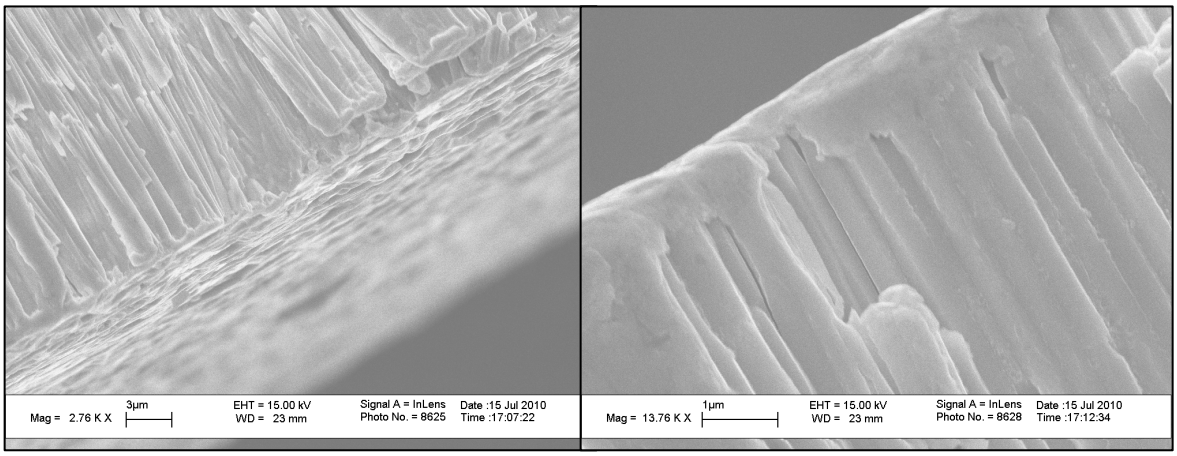


Figure 22: SEM Micrographs taken of the edge of sample 2/4/2010 T1/S2 in the non-heat treated ("as-received") condition at two magnifications showing zone I microstructure.

Differential Scanning Calorimetry

Figure 3 displays two DSC scans of sample 2/4/2010 T1/S2. The peaks are indicative of positive heat flow from the sample (exothermic reactions). Note the broad, small low temperature peak and the single, large symmetric peak at approximately 300 C/572^{o}F, in each. These two features are reproducible as can be seen in the two scans presented in the figure. The low temperature peak was seen in all non-heat treated samples.

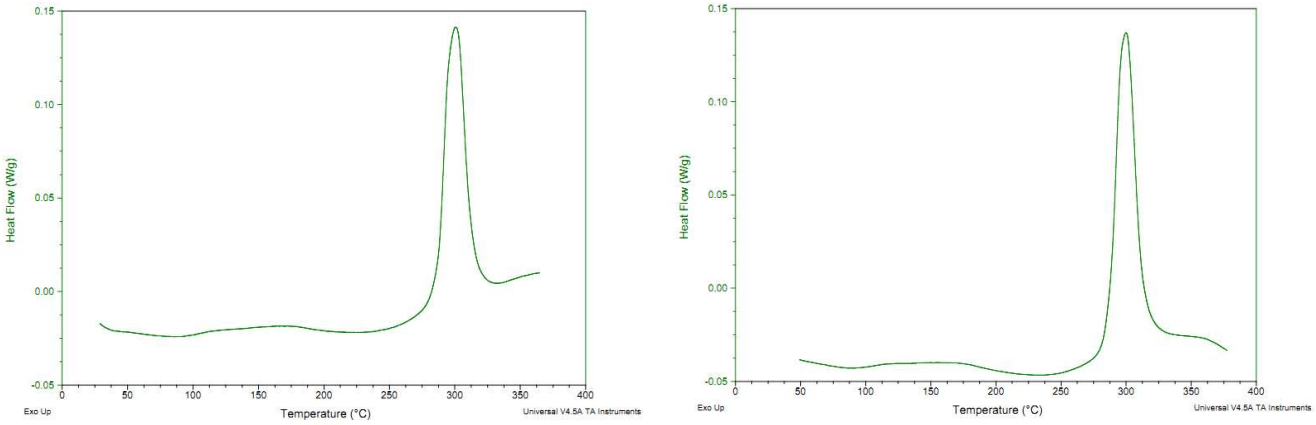


Figure 3: DSC scans from sample 2/4/2010 T1/S2 in the non-heat treated ("as-received") condition each displaying a broad low temperature peak and a symmetric high temperture peak.

Figure 4 displays a DSC scan from a portion of the same sample afer being heat treated to 200 C/392^{o}F. Note that most of the broad, low temperature is absent indicating that the change associated with this peak is non-reversible. The high temperature peak is essentially unchanged by the heat treatment.

The high temperature peak is essentially eliminated after heat treatment to 250 C/482 ^{o}F. Thus, this peak is indicative of a non-reversible transformation within the coating.

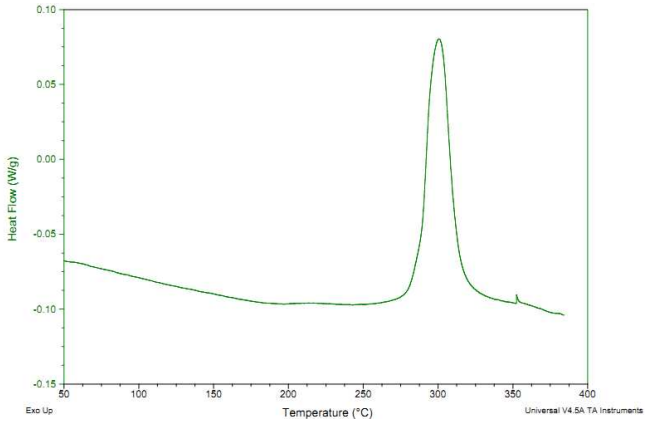


Figure 4: DSC scan from sample 2/4/2010 T1/S2 after heat treatment to 200 C/392^{o}F.

Other samples produced two high temperature DSC peaks as illustrated in figure 5 by two scans taken from sample 2/8/2010 T2/S1. The two high temperature peaks are centered about 275 C/527^{o}F and 305 C/581^{o}F. Note the broad, low temperature feature similar to that seen in figure 3. This peak is absent after heat treatments to 250 C/482 ^{o}F.

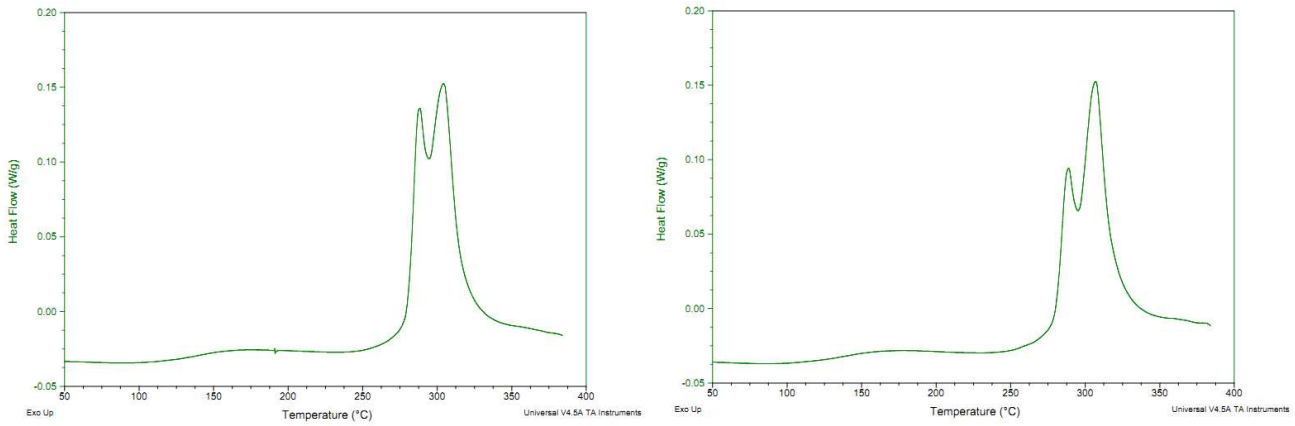


Figure 5: DSC scans from sample 2/8/2010 T2/S1 in the non-heat treated ("as-received") condition.

Other samples produced DSC traces displaying a single assymetric, high temperatur peak. Examples are shown for samples 12/8/2009 T2/S2 and 12/14/2009 T1/S2 in "as-received" condition in figure 6. In each the assemtric peak lies around 300 C/572^{o}F and each high temperature peak appears to have a "shoulder" on its low temperture side.

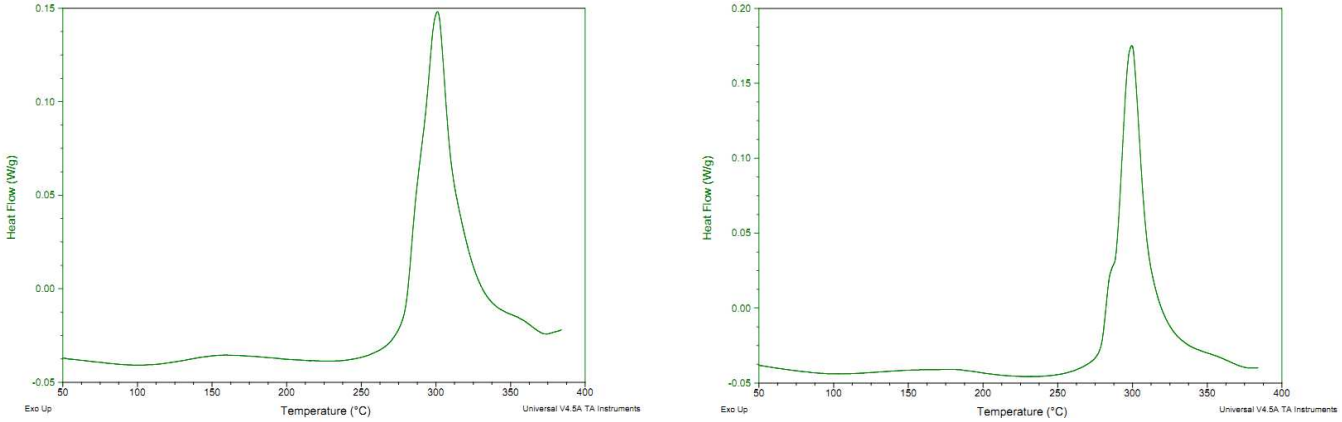


Figure 6: DSC scans from samples (left) 12/8/2009 T2/S2 and (right) 12/14/2009 T1/S2 in the non-heat treated ("as-received") condition. Note the asymmetric high temperture peaks.

Figure 7 displays the DSC data taken from sample 2/5/2010 T2/S1. (The scan was extended to 400 C/752^{o}F to capture the highest temperature peak.) This sample contained a extraordinary amount of lead, 2.08 wt%, whereas other samples had at most 0.72 wt%. There two widely separated, nearly symmetric peaks occuring at about 315 C (599^{o}F) and 386 C/727 ^{o}F that appear to overlap.

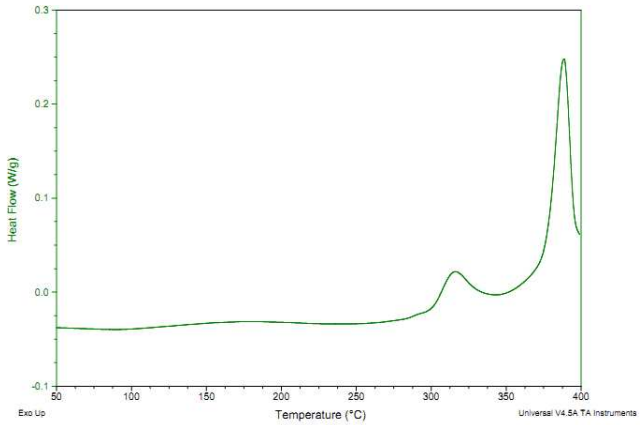


Figure 7: DSC scan from sample 2/5/2010 T2/S1 in the non-heat treated ("as-received") condition. Note the two high temperature peaks as well as the broad low temperature peak.

Table 2 lists the DSC results along with UCT Coatings provided compositions. Balance of compositions is Ni.

Table 2: DSC Results

Sample ID	**Composition (Wt%)**		**Peak(s)**	
	B	**Pb**	**Appearance**	**Maximum(s)**
12/8/2009 T2/S2	6.11	0.72	1 asymmetric	~300 C/572^{o}F + Low T shoulder
12/14/2009 T1/S2	5.98	0.67	1 asymmetric	~300 C/572^{o}F + Low T shoulder
1/18/2010 T2/S1	6.23	0.73	1 symmetric	~300 C/572^{o}F
2/4/2010 T1/S2	6.40	0.57	1 symmetric	~300 C/572^{o}F
2/5/2010 T2/S1	6.29	2.08	2 widely separated	~388 C/572^{o}F & ~319 C/606^{o}F
2/8/2010 T2/S1	6.06	0.58	2 overlapping	~288 C/550^{o}F & ~308 C/586^{o}F
3/1/2010 T1/S2	6.17	0.61	2 overlapping	~292 C/558^{o}F & ~304 C/579^{o}F
6/16 T2/S1	6.66	0.56	2 overlapping	~288 C/550^{o}F & ~308 C/586^{o}F

Microhardness

Table 3 below lists the average and standard deviation of microhardness results for sample CERT 61609 T2/S1, which contained a non-heat treated portion and a portion heat treated to 385 C/725^{o}F. There was no significant variation in hardness with indentation location.

Table 3: Microhardness Testing for CERT 61609 for "as-received" and Heat Treated Samples

CERT 61609 T2/S1	Non-Heat Treated Portion	Heat Treated to 385 C/725°F Portion
Average (Knoop)	959	1431
Standard Deviation (Knoop)	50.4	100.5

The Knoop calibration reference could not be located in the hardness testing lab. The machine was calibrated correctly for Vickers measurement prior to performing Knoop measurement. The average microhardness for the non-heat treated nickel boron cross section is 959 Knoop with a standard deviation of 50.4 Knoop. The average microhardness for the 385 C/725°F nickel boron cross section is 1431 Knoop with a standard deviation of 100.5 Knoop. The heat treated nickel boron coating shows a 49% increase in microhardness over the non-heat treated specimen.

X-ray Diffraction

XRD data from sample 2/5/2010 T2/S1 heat treated to 385°C/725 °F are displayed in Figure 8 as scattered x-ray intensity plotted versus scattering angle (2θ). The unspecified indexed peaks are for Ni_3B. Ni and Pb peaks are indicated explicitly.

Although this sample contains a high Pb content, its pattern displays all three of the crystalline phases identified in the various samples: Ni, Ni_3B and Pb. Unidentified peaks are indicated with a "?".

Figure 9 displays the results of a Rietveld analysis of these data indicating a phase content of 95.7% Ni3B, 3.6% Ni and 0.7% Pb. Rietveld analysis pertains only to crystalline phases and thus ignores the significant "amorphous hump" present in the data.

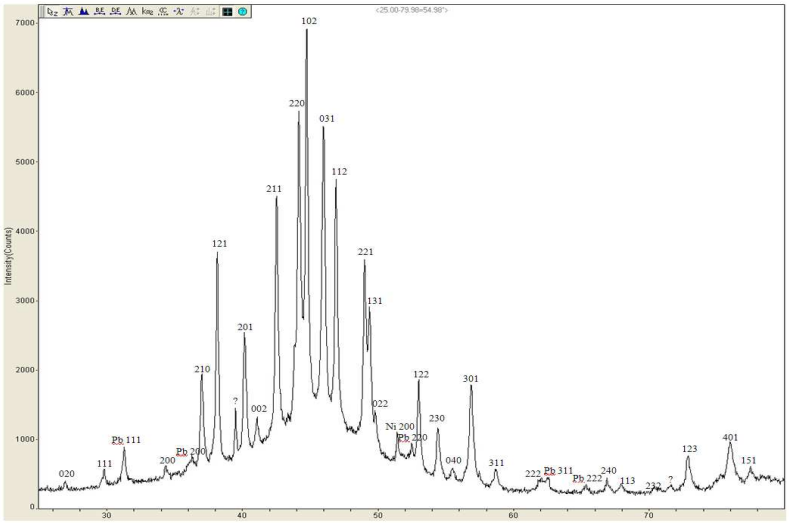


Figure 8: Indexed XRD pattern of 2/5/2010 T2/S1 (H.T. 385°C/725°F). Unlettered indices are for Ni_3B. Horizontal axes are 2θ.

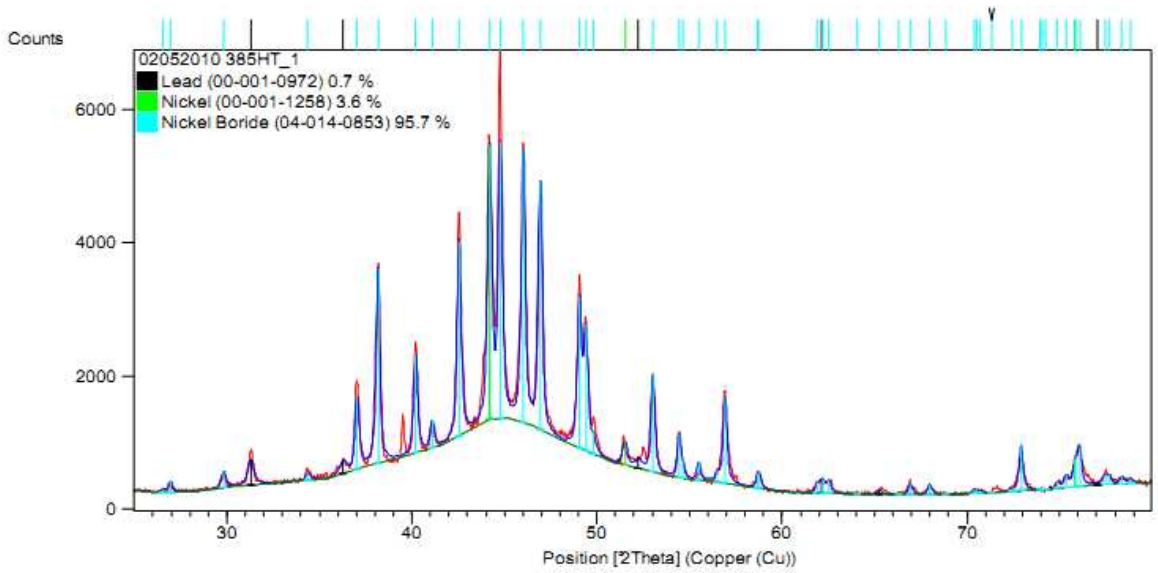


Figure 9: Result of Rietveld analysis of XRD data shown in figure 8: Sample 2/5/2010 T2/S1 (H.T. 385°C/725°F).

Figure 10 illustrates XRD data for sample 2/4/2010 T1/S2 in the non-heat treated ("as-received") condition, and after heat treatments of 300 C/572°F and 385 C/725°F.

The non-heat treated sample displayed a large "amorphous hump" often produced by amorphous material.

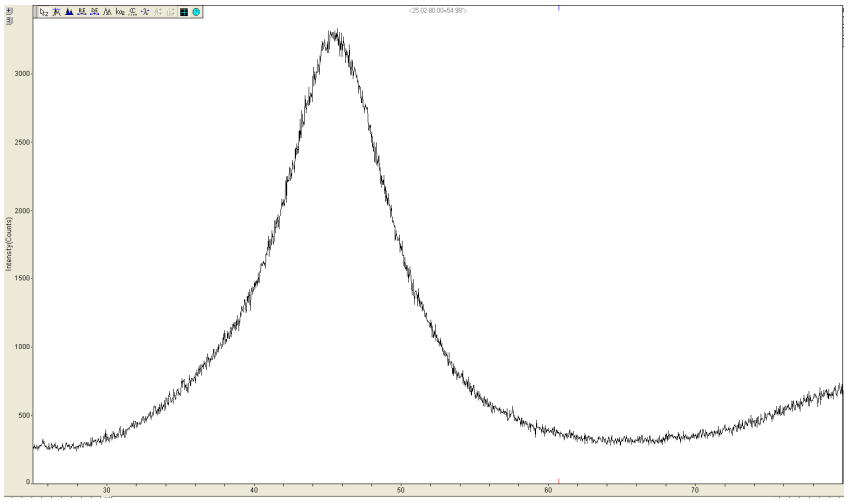
Figure 11 displays the results of a Rietveld analysis of these data indicating a phase content of 94.9% Ni_3B and 5.1% Ni. As mentioned above, Rietveld analysis ignores the "amorphous hump" present in the data. Figure 12 illustrates XRD data for sample 2/8/2010 T2/S1 in the non-heat treated ("as-received") condition, and after heat treatments of 300 C/572°F and 385 C/725°F.

Note the small crystalline peaks superimposed on the large "amorphous hump" of the non-heat treated sample. The apparent peak at $2\theta \sim 44.5^{o}$ near the top of the "amorphous hump" lies near the position of the Ni (111) peak, the strongest Ni peak. The three peaks seen at $2\theta \sim 25.5^{o}$, 35^{o} and 45.5^{o} have not been identified (see below).

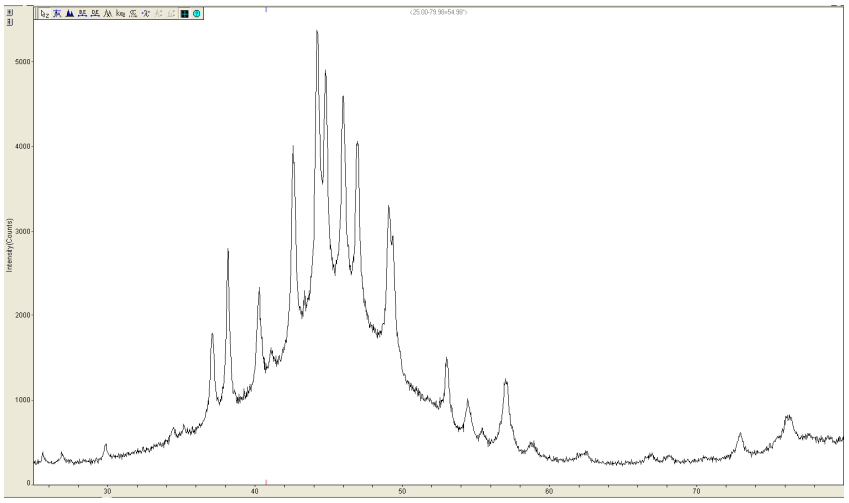
Figure 13 displays the results of a Rietveld analysis of these data indicating a phase content of 97.6% Ni_3B and 2.4% Ni. As mentioned above, Rietveld analysis ignores the "amorphous hump" present in the data.

Table 4 presents results of the Rietveld analysis of the three samples subjected to the full heat treatment regimen.

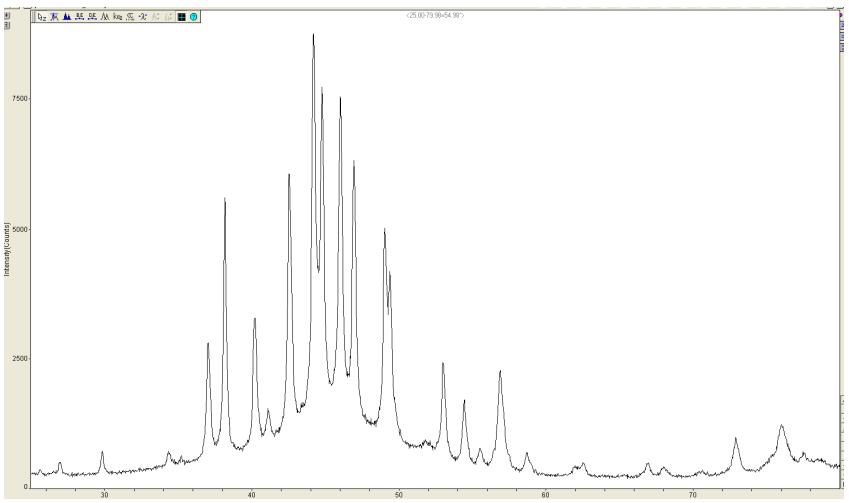
Several very weak to moderate intensity peaks were seen that could not be identified using the ICDD PDF-4+ 2010 powder diffraction database. Tables 5 – 7 detail the positions and relative intensities of these unidentified peaks in samples 2/4/2010 T1/S2, 2/5/2010 T2/S1, and 2/8/2010 T2/S1, respectively.



Non-H.T.



300 C/572°F H.T.



385 C/725°F H.T.

Figure 10: X-ray diffraction pattern of 2/4/2010 T1/S2 in the non-heat treated ("as-received"), heat treated to 300 C/572°F and 385 C/725°F. Horizontal axes are 2θ.

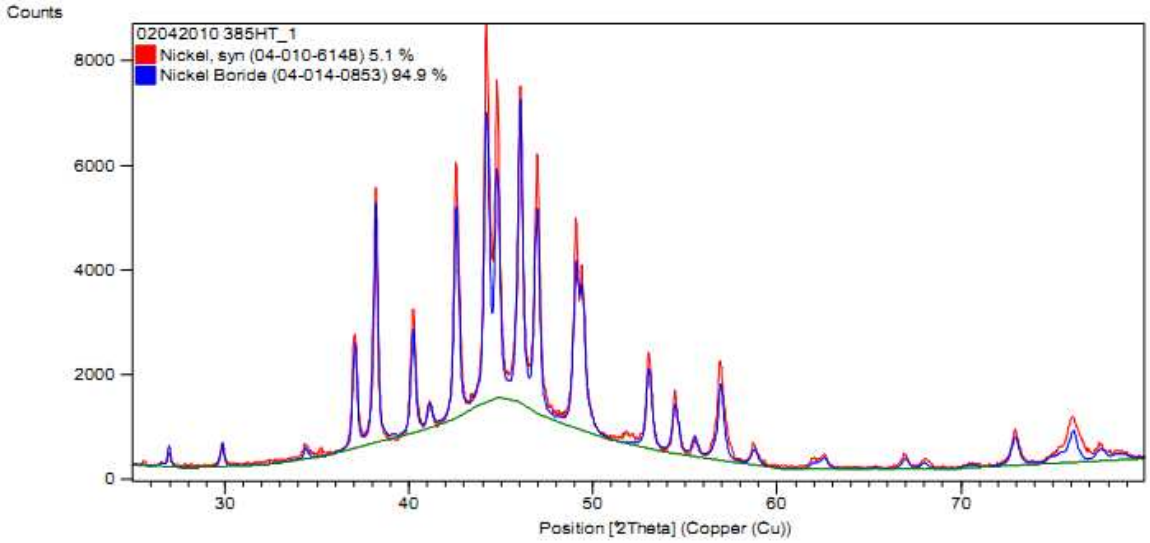


Figure 11: Result of Rietveld analysis of XRD data shown in the lower frame of figure 10: Sample 2/4/2010 T1/S2 (H.T. 385°C/725°F).

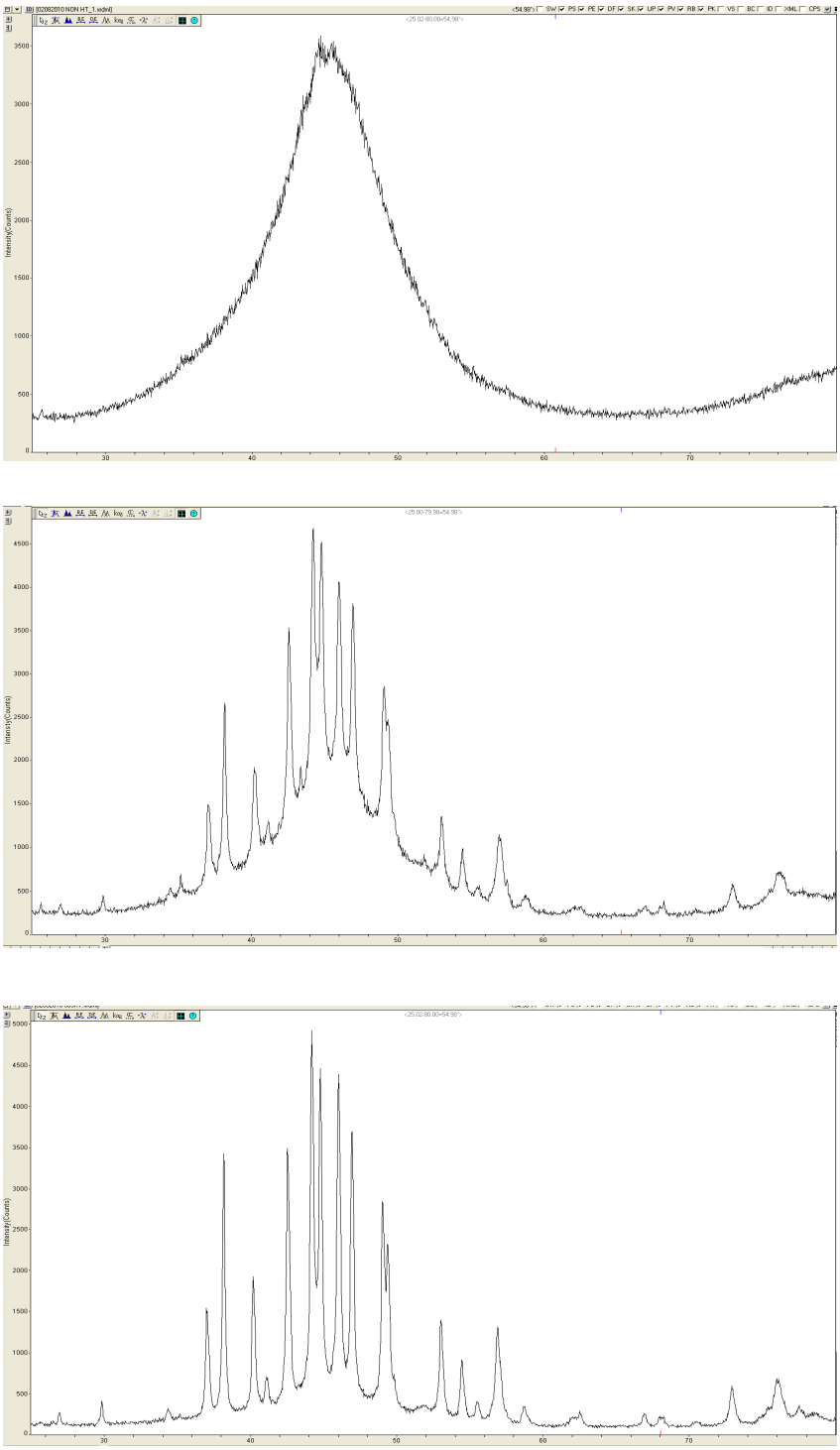


Figure 12: X-ray diffraction pattern of 2/8/2010 T2/S1 in the "as-received," heat treated to 300°C and 385°C condition. Horizontal axes are 2θ.

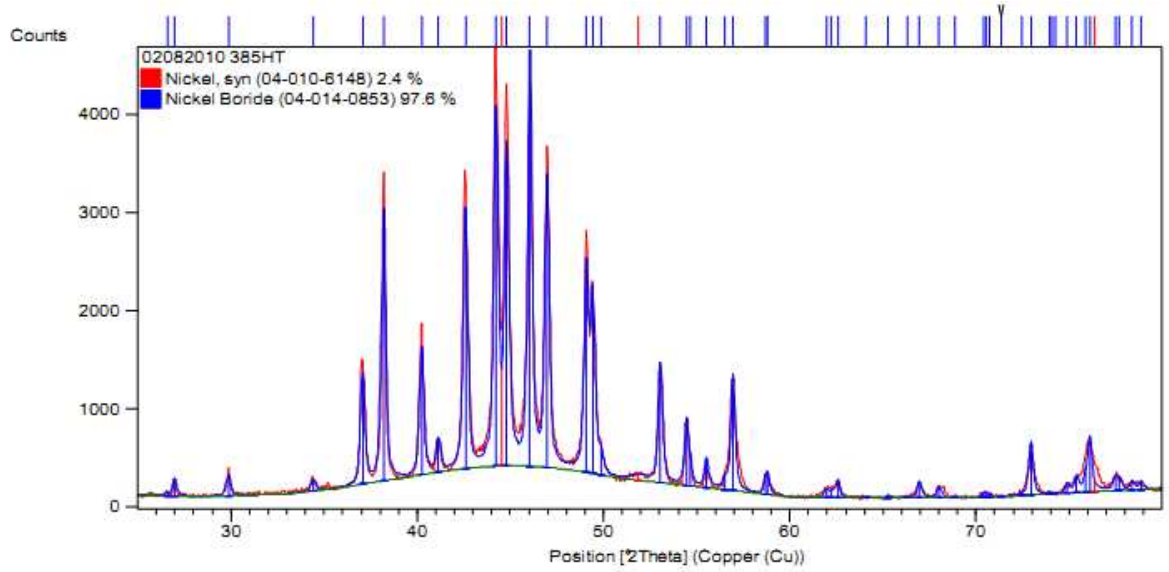


Figure 13: Result of Rietveld analysis of XRD data shown in the lower frame of figure 12: Sample 2/8/2010 T2/S1 (H.T. 385°C/725°F).

Table 4: Results of Rietveld Analysis of Three Samples

Sample	Heat Treatment (C/°F)	Crystalline Phase Content* (volume %)			Comments
		Ni_3B	Ni	Pb	
02/04/2010 (T1/S2)					Single symmetric DSC peak
	250/482				Ni (111) & small unknown pks. on "Amorphous Hump"
	275/527		100		Ni pks. on "Amorphous Hump"
	300/572	100			
	325/617	100			
	350/662	100			
	385/725	94.9	5.1		
02/05/2010 (T2/S1)					2 widely separated DSC peaks; High Pb content sample
	250/482				Ni (111) & small unknown pks. on "Amorphous Hump"
	275/527			trace	
	300/572	80.9	16.2	2.9	
	325/617	99.9		0.1	
	350/662	99.6		0.4	
	385/725	95.7	3.6	0.7	
02/08/2010 (T2/S1)					2 overlapping DSC peaks
	250/482				Ni and unknown pks on "Amorphous Hump"
	275/527		100		Ni pk. on "Amorphous Hump"
	300/572	~100	trace		
	325/617	100			
	350/662	93.9	6.1		
	385/725	97.6	2.4		

Table 5: Summary of Unidentified XRD Peaks Produced by Sample 2/4/2010 T1/S2

H.T. (C/^{o}F)	Peaks Key: vs w - weak; vw - very weak; Interplanar d spacings in Angstroms.	
	d~3.49 2θ~25.5^{o}	d~2.56 2θ~35^{o}
None	vw	vw
300/572	w	vw
325/617	vw	vw
350/662	vw	vw
385	w	w

Table 6: Summary of Unidentified XRD Peaks Produced by Sample 2/5/2010 T2/S1

H.T. (C/^{o}F)	Peaks Key: m - moderate; w - weak; vw - very weak; nd - not detected Indices are listed where appropriate. Interplanar d spacings in Angstroms. "?" indicates uncertainty in peak presence.			
	d~3.49 2θ~25.5^{o}	d~2.56 2θ~35^{o}	d~2.08 2θ~43.4^{o}	d~1.99 2θ~45.5^{o}
None	w	vw	nd	vw ?
300/572	w	w	m	nd
325/617	w	w	nd	nd
350/662	nd	nd	nd	nd
385/725	vw	vw	nd	nd

Table 7: Summary of Unidentified XRD Peaks Produced by Sample 2/8/2010 T2/S1

H.T. (C/^{o}F)	Peaks Key: m - moderate; w - weak; vw - very weak; nd - not detected Indices are listed where appropriate. Interplanar d spacings in Angstroms.			
	d~3.49 2θ~25.5^{o}	d~2.56 2θ~35^{o}	d~2.28 2θ~39.5^{o}	d~1.32 2θ~71.4^{o}
None	vw	w	nd	nd
300/572	w	vw	nd	nd
325/617	vw	vw	nd	nd
350/662	nd	nd	nd	nd
385/725	nd	nd	m	w

Hot Stage XRD

Hot Stage XRD data from sample 12/8/2009 T2/S2 collected during a heat treatment to 385 C725°F are displayed in Figures 14 and 15. These data are displayed with increasing temperature (room temperature is at the bottom to 385 C/725°F at the top). The data were taken with cobalt radiation, and thus the 2θ angles differ from those collected with copper radiation.

All peaks present can be attributed to either Ni or Ni_3B. Peak position indicators (pdf card overlay) for the latter phase are superimposed on figure 14. The largest peak near $2\theta \sim 53.7^{o}$ is 031 Ni_3B, its most intense. The two indicated Ni_3B peaks to its immediate left bracket the 111 Ni peak, Ni's most intense. Note the increase in the Ni (111) peak intensities at the highest temperatures and the development of a low angle shoulder on the Ni_3B (031) peak at the highest temperature, possibly evidence of a Ni_2B (211) peak (its strongest). Figure 15 offers a magnified view of these peaks.

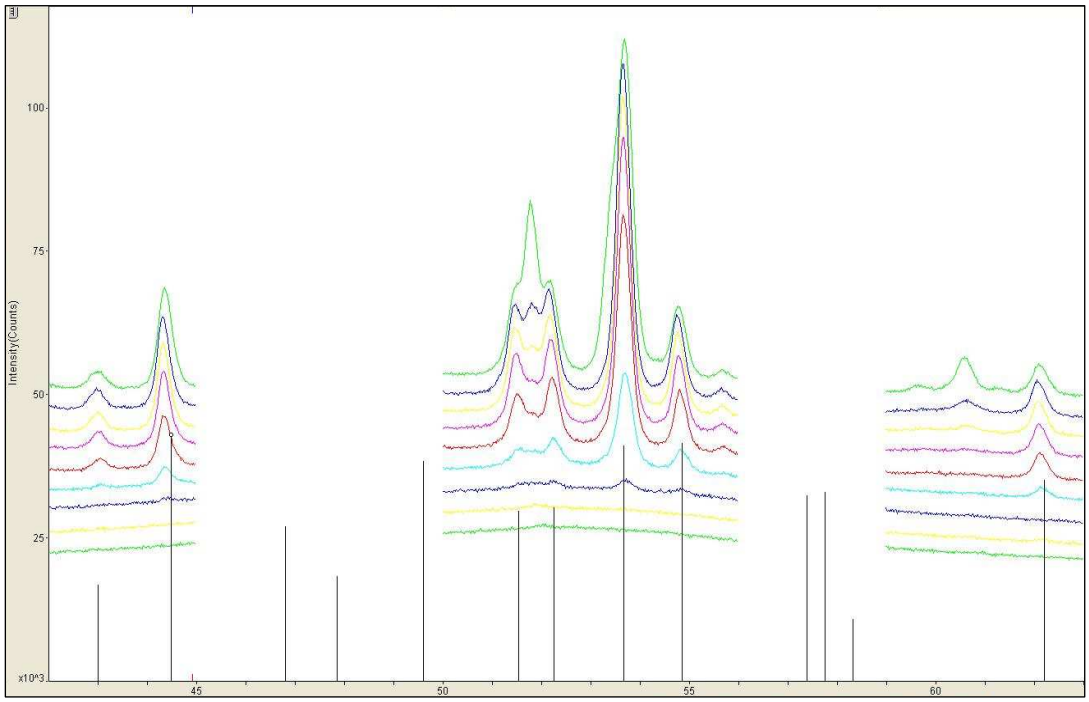


Figure 14: X-ray diffraction pattern over incremental heat treatments of sample 12/8/2009 T2/S2 with Ni_3B peak position indicators. The largest peak is sloely 031 Ni_3B, except possibly at the highest temperature (see text).

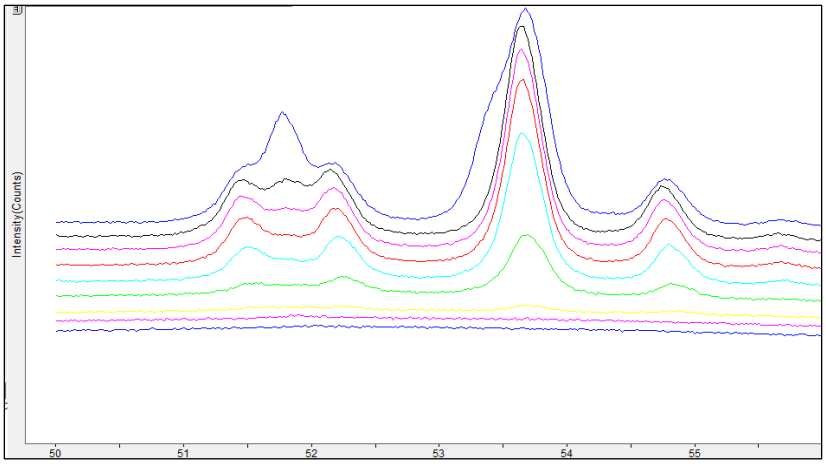


Figure 15: Detail of x-ray diffraction pattern from figure 14. Note Ni (111) peak ($2\theta \sim 51.8^o$) growth at high T (upper curves) and low angle shoulder on the highest T Ni_3B (031) peak ($2\theta \sim 53.7^o$) possibly due to Ni_2B (211).

Small Angle X-ray Scattering

Small angle x-ray scattering data were reduced to Guinier plots (natural logarithm of the scattered x-ray intensity versus $16\pi^2\theta^2/\lambda^2$; with units of radians for θ). Data producing a negatively sloped straight line at low scattering angles may be interpreted as scattering by 'particles' whose radius of gyration squared is the negative of the slope of the line. 'Particles' are regions within the sample with a larger scattering/electron density than the matrix in which they are embedded.

Figure 16 below displays the Guinier plots of two samples. Table 8 displays the results for the six samples examined including the transverse radii of the scattering 'particles' assuming that they are uniform columns of circular cross section aligned with the incident x-ray beam (see SEM data above).

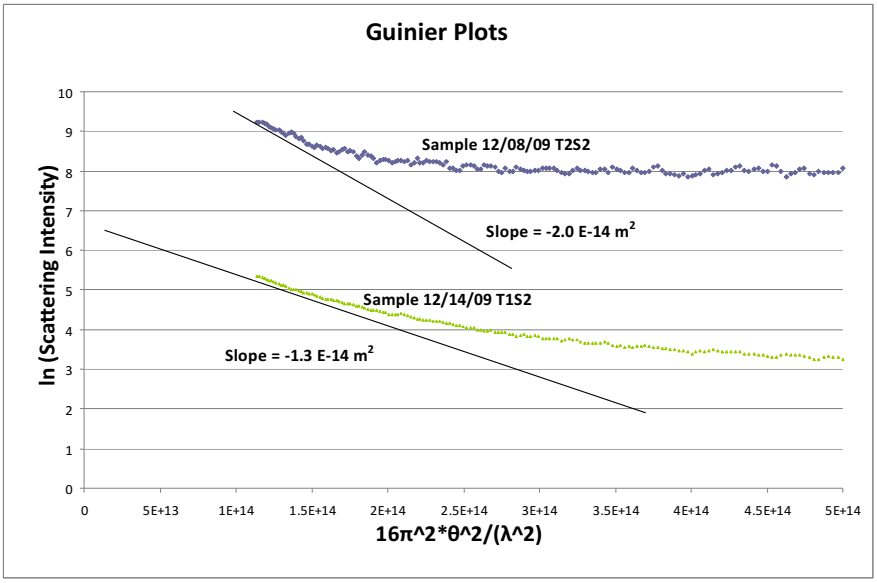


Figure 16: Guinier plots of small angle x-ray scattering data from two samples in the "as-received" condition.

Table 8: Small Angle X-ray Scattering Results

Sample ID	Slope of Guinier Plot (m^2)	Average Inertial Distance along Transverse Diameters of Columnar "Particles"* (nm)	Transverse Radii of Columnar "Particles" (nm)
12/08/09 T2S2	-2.0×10^{-14}	140	280
12/14/09 T1S2	-1.3×10^{-14}	115	230
1/18/10 T2S1	-1.6×10^{-14}	130	260
2/4/10 T1S2	-1.2×10^{-14}	110	220
2/5/10 T2S1	-1.2×10^{-14}	110	220
2/8/10 T2S1	-1.1×10^{-14}	100	200

* X-ray beam aligned with axial direction of columns of circular cross section (See SEM data above.)

Extended XRD of Non-Heat Treated Samples

Extended data collection time x-ray diffraction patterns were collected from three of the samples examined by SAXS: 12/08/2009 (T2/S2), 12/14/2009 (T1S2), and 1/18/2010 (T2/S1) in their non-heat treated ("as-received") condition. Figure 17 displays such a pattern collected from sample 1/18/2010 (T2/S1). Note the "amorphous humps" and the superimposed crystalline peaks, which are due to Ni.

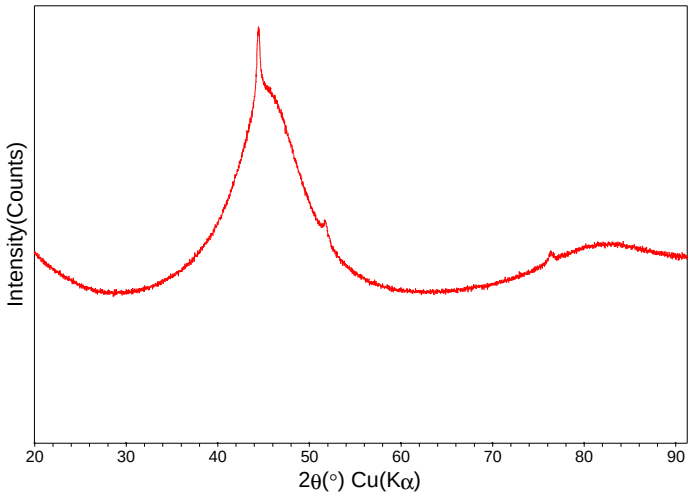


Figure 17: Extended XRD scan of sample 1/18/2010 (T2/S1) in the "as-received" (non-heat treated condition). The crystalline peaks superimposed on the amorphous background are due to Ni.

The MDI JADE 9 was used to peak fit the large "amorphous hump" and the two superimposed nickel peaks [(111) and (200)]. Figure 18 illustrates the graphical result of the fitting process.

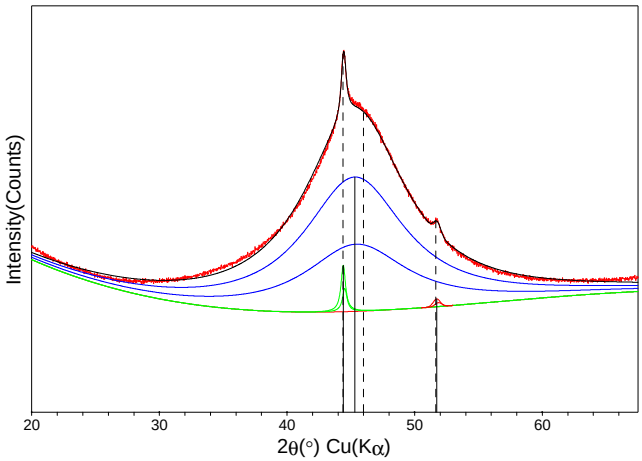


Figure 18: Fitting result produced by JADE software on "amorphous hump" produced by sample 1/18/2010 (T2/S1) in the "as-received" (non-heat treated condition).

Table 9 displays results produced by the JADE software, particle sizes based on widths of Ni (111) and Ni (200) peaks. This contains estimates of particle size made with the Scherrer formula. These size estimates exclude peak broadening due to strain and thus should be regarded as lower limits. The disagreement suggests the crystallites are inhomogeneously strained as a given amount of strain produces greater peak broadening at larger scattering angles, and thus narrower peaks that appear to have been produced by smaller particles.

Percent crystallinity is also estimated by the software based on the relative areas of the "amorphous hump" and the crystalline peaks. The assumption is that the "amorphous hump" is due to amorphous material with a scattering density similar to that of the crystalline material. The latter is perhaps not a bad assumption if one ignores the Pb present (0.73 wt% in 1/18/2010 (T2/S1), less in others).

Table 9: Peak Fitting Results from Extended XRD Scans of "as-received" (non-heat treated) Samples. Particle Sizes are Estimates from Ni(111) and (200) Peak Widths.

Sample ID	Particle Size (nm)		% Crystallinity (Estimate)
	Ni(111)	Ni(200)	
12/08/2009 (T2/S2)	8	-	2
12/14/2009 (T1S2)	29	18	2
1/18/2010 (T2/S1)	23	15	2

Discussion

SEM micrographs show a "cauliflower-like" structure consisting of bundles of small (200 – 400 nm diameter) columnar structures. The "nodules" visible in lower magnification plan views may be related to the grain structure of the substrates from which the coatings were removed.

The coatings have the appearance of zone I coatings as described by Movchan and Demchishin[1] for evaporated metal coatings deposited at substrate temperatures less than 0.3 T_m (T_m being the melting temperature of the coating in degrees K) and Thornton for sputtered metal films at similar low deposition temperatures.[2] That is the coating consists of columnar structures separated by voided boundaries of several nanometers in width. Zone I films are reported as appearing "cauliflower-like." Zone I structures are expected to have little lateral strength.

The principal feature in the XRD data from the θ–2θ scans taken after all but the highest heat treatments is the large, broad "amorphous hump" centered near a 2θ corresponding to the Ni (111) peak (2θ~46°). This is indicative of either amorphous and/or nano-crystalline structure.

Several small Bragg peaks, including Ni peaks, are superimposed on these "amorphous humps" for the non-heat treated ("as-received") coatings. The Ni peaks eventually disappear after low temperature heat treatments only to reappear at the highest treatment temperatures. Long duration XRD scans of non-heat treated samples indicate the Ni crystals are no smaller than ~ 8 – 30 nm. Since any inhomogeneous strain in the crystals would contribute to peak broadening, these numbers are underestimates.

Coatings heat treated beneath 300 C/572^{o}F display no boride peaks. Samples heat treated to at least 300 C/572^{o}F have significant crystallinity that is dominated by Ni_3B.

The small angle x-ray scattering was performed in an attempt to detect scattering from possible nanocrystalline regions within amorphous material. However, SAXS appears to have detected the columnar structures within the coatings and to confirm what is most readily evident from SEM, including boundaries between the columnar structures that are less dense than the structures themselves. Any small angle x-ray scattering from features of smaller size was not seen and would, if present, be difficult to detect.

The broad, small low temperature peak between ~100 C/212 ^{o}F to ~ 200 C/392 ^{o}F appears in all DSC scans of non-heat treated ("as-received") samples. This is hypothesized to be due to processes similar to recovery that occurs prior to recrystallization in cold worked metals. In crystalline material, recovery involves motion of vacancies and the rearrangement of dislocations (polygonization) in crystalline material. This may be occuring in the Ni crystals. High intrinsic stress, and accompanying defects, is expected in zone I coatings due to their low deposition temperatures.

[1] B.A. Movchan & A.V. Demchishin, *Phys. Met. Metallogr.* **28**, 83 (1969).
[2] J.A. Thornton, *Ann. Rev. Mater. Sci.* **7**. 239 (1977).

Recovery in crystalline materials is known to be associated with significant softening. Thus, a hardness v. heat treat temperature study is a possible means of further classifying this process.

Consider the DSC data of nickel deformed in tension and heated at 6 C/ 10.8^{o}F per min. shown in figure 23.[3] The lower temperature exothermic peak, which reaches a maximum at about 240 C/464^{o}F, is due to recovery processes. The high temperature peak (~590 C/1,094 ^{o}F) is due to Ni recrystallization (far above any temperature reached in the current work).

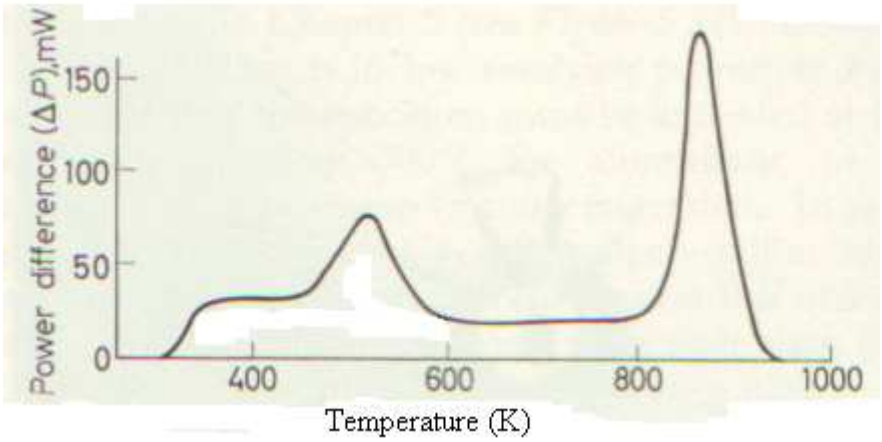


Figure23: DSC data of nickel deformed in torsion and heated at 6 C/min. Taken from Clareborough et al.[3]

Two samples appear to undergo a single high temperature exothermic reaction, as indicated by a single symmetric peak in each of their DCS spectra (see Table 2). However, other samples of similar composition display either asymmetric or overlapping exothermic peaks at nearly the same temperature.

The sample examined with high Pb content displays two distinct (non-overlapping), high temperature, exothermic reactions. These are perhaps indicative that the two reactions seen at lower temperatures in other samples are inhibited by the presence of lead. Observable crystalline lead formed in this sample with a heat treatment as low as 275 C/527^{o}F, well below the DSC peak at ~319 C/606 ^{o}F.

Thus, in addition to a low temperature, recovery-like process, at least two separate higher temperature reactions occured within most samples, although their relative intensities vary significantly.

Based on the data collected, it is not possible to identify the reactions associated with the two high temperature DSC peaks, nor to determine whether two spearate reactions or a single reaction occur in samples displaying a single symmetric high temperature DSC peak.

One can speculate that the reported compositional differences between samples are responsible for the diverse DSC behavior. Certainly excess lead seems to have such an effect and the presence of unidentified XRD peaks are further evidence of compositional variation.

[3] Clareborough, Hargraves & West, *Proc. Roy. Soc.* **A232**, 252 (1955).

XRD examination of samples heat treated to various temperatures (at and between those of the high temperature DSC peaks) and immediately quenched would provide a means of identifying the reactions associated with each DSC peak.

An asymmetric DSC peak (between 306 C/582.8^{o}F and 333 C/631.4 ^{o}F) has been previously reported for electroless Ni-B coatings deposited from thallium stabilized baths.[4] The authors attribute it to the formation of Ni_3B. They also report the formation of Ni_2B at temperatures around 430 C/806^{o}F in coatings containing more than 20 atomic % (4.4 wt %) B.

No evidence of Ni_2B was detected in any XRD data collected here, with the single possible exception of the hot stage XRD data. These show a substantial increase in the intensity of the Ni (111) peak at the highest temperatures and the formation of a low angle shoulder on the Ni_3B (031) peak at only the highest observation temperature. This latter feature is perhaps due to Ni_2B (211). The formation of Ni_2B is expected to be accompanied by the release of Ni from Ni_3B.

Keeping in mind that all heat treatments resulted in over-aging due to furnace cooling, whereas DSC results are more "temperature accurate," the following can be surmised from the DSC and XRD data:

- A low temperature "recovery" process occurs between ~100 C/212 ^{o}F to ~ 200 C/392 ^{o}F.
- Small amounts of crystalline Ni, and either amorphous Ni-B or nanocrystalline material, is replaced by Ni_3B by about 300 C/572^{o}F.
- Small amounts of crystalline Ni reappear at the higher annealing temperatures in the presence of Ni_3B (without detectable amounts of Ni_2B).

Conclusions

- As deposited coatings display a Zone I type morphology characterized by columnar structures ~200 – 500 nm in diameter oriented approximately normal to the plane of the coatings.
- The columnar structures are not single grains, but are rather composed of amorphous material and/or nanocrystalline grains separated by less dense boundaries.
- UCT Heat treatment produces a hardness increase of 49%.
- Ni_3B was present in all coatings heat treated to at least 300 C /572^{o}F.
- Full heat treatments (to 385 C/725^{o}F) produced Ni_3B and crystalline Ni, with some amorphous/nanocrystalline material remaining.
- A low temperature (~100 C/212 ^{o}F to ~ 200 C/392 ^{o}F) exothermic reaction occurs in the coatings that mimics the thermal effects of recovery in cold-worked Ni.
- Two higher temperature (~300 C/572^{o}F and above) exothermic reactions occur in some coatings with varying amounts of temperature overlap, whereas other coatings display only a single such reaction.
- One of these higher temperature reactions is most assuredly associated with the formation of Ni_3B.
- The second higher temperature reaction was not identified.

[4] T.S.N. Sankara Narayanan & S.K. Seshadri, *J. Alloys & Comps.* **365**, 197 (2004).

- Crystalline Pb was produced by all heat treatments to 300 C/572^{o}F and above in a sample containing 2.08 wt% Pb. No other sample (0.58 wt% Pb max) displayed crystalline Pb.
- Unidentified phases were observed in several coatings.